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Excess free volume of binary liquid mixtures

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Excess free volumes for the systems benzene + ethanol, benzene + *iso*-propanol, benzene + *n*-heptane, benzene + *n*-hexane, carbon tetrachloride + *o*-xylene, carbon tetrachloride + *m*-xylene, carbon-tetrachloride + *p*-xylene, toluene + *o*-xylene, toluene + *m*-xylene and toluene + *p*-xylene have been determined with the help of measured ultrasound velocity. Both positive and negative deviations have been observed. The results have been interpreted on the basis of molecular interaction forces.

1. INTRODUCTION

Eyring *et al* (1937) described that molecules in the liquid state are so loosely packed as to leave some free space between them and this free space is known as free volume (V_f). The free volume is defined by Eyring *et al* (1937) as the effective volume in which a particular molecule of the liquid can move and obey the perfect gas law. Eyring *et al* (1937a, 1938b) have given the following equation relating molar volume (V), sound velocity in vapour (v_g) and sound velocity in liquid (v) with free volume (V_f) as

$$V_f = V \left(\frac{v_g}{v}\right)^3 . \qquad (1)$$

The above equation has been applied to calculate the free volume in pure liquids as well as in liquid mixtures. From eq (1) free volume (V_f) can be calculate if v_g is known. The experimental value of v_g is not dependable due to the velocity dispersion which is caused by the thermal relaxation in the vapours and so static value of v_g obtained by eq (2) has been used for the calculation of free volume (V_f).

$$v_g = \left[\frac{C_p}{C_v}\frac{RT}{M}\left\{1+\frac{9}{128}\frac{p}{p_c}\cdot\frac{T_c}{T}\left(1-6\frac{T_c^2}{T^2}\right)\right\}\right]^{\frac{1}{2}} \qquad \ldots \quad (2)$$

where R is the gas constant in ergs. M is the molecular weight, T is the absolute temperature, p is the pressure in atmosphere, T_c and p_c are the critical temperature and pressure. C_p and C_v of the vapour are calculated by the expression given by Dobratz (1941).

$$C_p = C_v + R\left[1+\frac{81}{32}\frac{p}{p_c}\left(\frac{T_c}{T}\right)^3\right] \qquad (3)$$

and,

$$C_v = 3R + \frac{aR}{2} + \Sigma q_i C_{\nu i} + \frac{3n-6-a-\Sigma q_i}{\Sigma q_i} \Sigma q_i C_{\delta i} \quad \ldots (4)$$

where R is the gas constant in calories, n is the number of atoms in the molecule, a is the number of bonds in the molecule permitting free rotations of groups; q_i is the number of bonds of ith type; $C_{\nu i}$ and $C_{\delta i}$ are the Einstein functions at frequencies ν_i and δ_i respectively for the ith type of bonds and are evaluated by the quadratic eq (5) given by Fugassi *et al* (1938)

$$C_i = A + BT + CT^2 \quad (5)$$

The constants A, B and C for different bonding frequencies are listed in Table by Dobratz (1941)

As an approximation v_g for the mixtures of vapours have been assumed to be additive The value of v_g for the mixture has been calculated by—

$$(v_g)_{mix} = X_1 v_{g1} + X_2 v_{g2} \quad \ldots (6)$$

The excess free volume (V_f^E) is calculated from the following relation—

$$V_f^E = (V_f)_{mix} - (X_1 V_{f1} + X_2 V_{f2}) \quad \ldots (7)$$

where X_1 and X_2 are the mole fractions of the two components of the liquid mixtures and V_{f1} and V_{f2} are their free volumes respectively.

Deshpande & Bhatgadde (1968) calculated for the first time the free-volume in six binary mixtures with aniline as common component Prakash *et al* (1972-75) calculated free volume in ternary mixtures Former authors observed negative deviations from ideality in five and positive in only one They had used only one non-polar liquid and none was associating Keeping this in mind polar, non-polar and associating liquids were used to get the combinations of different nature, i.e., polar-non polar, non polar-non polar, non-polar–polar and associating Toluene which has only small dipole moment (0 4 D) can be taken to be non-polar. Ten mixtures were studied to learn more about their behaviour with regard to free volume and possible interactions

The systems studied are—benzene + ethanol (35°C), benzene + *iso*-propano (35°C), benzene + *n*-heptane (25°C), benzene + *n*-hexane (23°C) carbon tetrachloride + *o*-xylene (30°C), carbon tetrachloride + *m*-xylene (23°C), carbon tetrachloride + *p*-xylene (23°C), toluene + *o*-xylene (30°C), toluene + *m*-xylene (30°C), toluene + *p*-xylene (30 C) The free volumes were calculated from eq (1) and by measuring the ultrasound velocity v in pure liquids and their mixtures, and calculated r_g from eq (2)

2. Experimental Procedure

Liquids used were (BDH, AR) and were redistilled and purified by standard methods described by Weissberger (1959) The densities were measured by the density bottle, and those of pure liquids agreed closely with the literature values The mixtures of liquids for different mole fractions were prepared by adding the appropriate volume of each other in the well cleaned and dried measuring flasks. The solutions were kept for some time stabilization and then transferred to the ultrasonic cell for the measurement of ultrasonic velocities The temperature of the cell was maintained at constant temperature by circulating water from a thermostatic bath Ultrasonic velocities at the frequency of 5 MHz have been measured by the light diffraction method of Debye & Sars (1932) The source of ultrasonic waves was a generator comprising an oscillator unit and a gold plated circular quartz crystal of 2.54 cm diameter as transducer A suitably designed optical cell by Prakash *et al* (1966) was used for containing the solution and with help of a filter, light of wave length 3657 Å from a mercury vapour lamp allowed to fall normally to the path of the ultrasonic waves Such waves transversing in a liquid set up a periodical inhomogeneity which acts as an optical grating The diffraction patterns were photographed on a orthochromatic Agfa plates and fringe distances were measured by a comparator made by M/S Adam Hilga Ltd., London, reading upto fourth place of decimal The probable error in the measurement of velocity is ±0 20%

3 Results and Discussion

The results have been presented in the form of graphs in figures 1–3. These figures give a qualitative picture of the excess free volume for binary liquid mixtures at the given temperatures The curves indicate the extent of deviation from ideality with the molar composition of the mixtures The excess free volume increases first, passes through maximum and then decreases in benzene + *iso*-propanol (figure 1), benzene + *n*-heptane (figure 3), carbon tetrachloride + *p*-xylene (figure 1) and toluene + *p*-xylene (figure 2) They are all oconcave to the mole fraction, axis, i e , the excess free volume is positive for these four systems Physical interactions between unlike molecules are usually weak and give rise to +ve deviations The results are indicative of weak interactions, involving dispersion forces between the molecules of these systems On the other hand, in case of benzene + ethanol (figure 1) toluene + *o*-xylene (figure 2) and carbon tetrachloride + *m*-xylene (figure 2) the excess free volume is negative which shows the existence of strong interactions between the components of these three systems In the remaining three systems reported here the excess values are found to be both positive and negative In the case of benzene + *n*-hexane system (figure 3), V_f^E is positive when the mole fraction of benzene is low and becomes negative when benzene is present in excess. In case of toluene + *m*-

xylene (figure 2) and carbon tetrachloride-+-*o*-xylene (figure 3) behaviour is such that a negative V_f^E is found at lower mole fraction of carbon-tetrachloride in

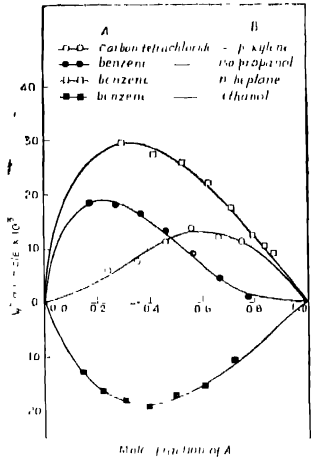

Fig 1 Plot of excess free volume vs composition of the mixture.

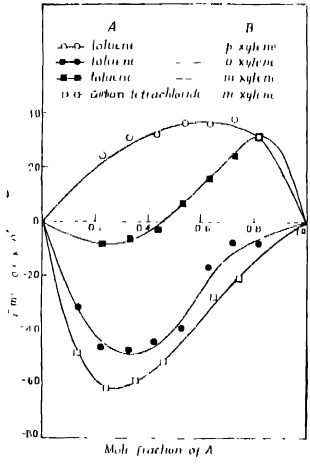

Fig. 2. Plot of excess free volume vs composition of the mixture

former and toluene in latter The nature of sign changes when the mole fractions

of these components are increased. This shows that there is a decrease in the strength of interaction between components of these mixtures with increase in the mole fraction of carbon tetrachloride in former case and toluene in the latter

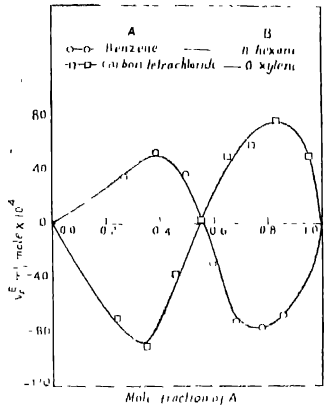

Fig 3 Plot of excess free volume vs composition of the mixture

According to Fort *et al* (1965) the excess free volume tends to decrease and then becomes increasingly negative as the strength of the interaction between the unlike molecules increases, although they do not parallel the excess compressibilities The change from positive to increasingly negative excess values as the strength of the interaction between the components increases may be interpreted in terms of closer approach of unlike molecules leading to reduction of compressibility and volume

Dispersion forces, which are likely to be operative in every case, should make positive contribution to excess values The specific or chemical interactions may lead to formation of complexes or molecular compounds between the components of the mixture This may involve charge transfer, dipole-dipole interactions and hydrogen bonding and should make negative contributions The magnitude of contributions made by these different types of interactions will vary both with the components and the composition of the mixtures.

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